Hydrogen-Bonding Surfaces for Ice Mitigation

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Background

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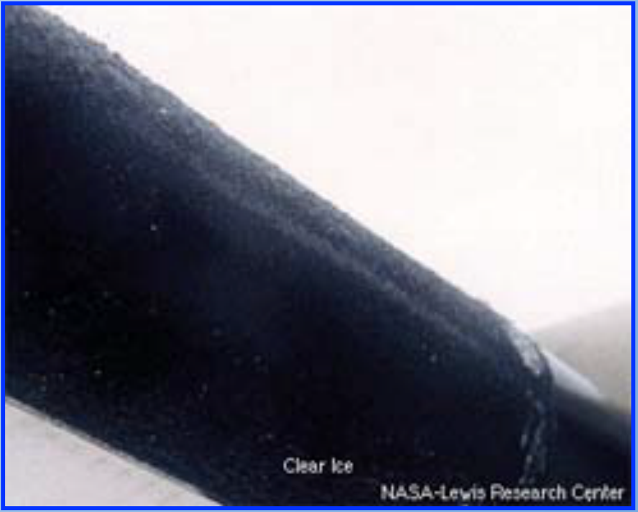
- Icing
  - Ground problem during cold months.
  - In-flight problem year round.
  - Results from super-cooled water droplets impacting the aircraft surface.
  - Most occurrences are between 0 and -20°C.

- Icing types
  - Dependent upon air temperature (-5 to -20°C), liquid water content (0.3-0.6 g/m^3), and droplet size (median volumetric diameter of 15-40 μm).

  - Glaze/Clear:
    - large droplets.
    - appearance is clear, nearly transparent, smooth, waxy thus hard to see.
    - gradual freezing after droplet impact can result in runback along surface generating horns (i.e. raised edges).
    - difficult to remove.



M.K. Politovich, "Aircraft Icing" in Encyclopedia of Atmospheric Sciences, Academic Press, Oxford, 2003, 68-75.
H.E Addy Jr., M.G. Potapczuk, and D.W. Sheldon, "Modern Airfoil Ice Accreations", NASA TM 107423, 1997.

Background

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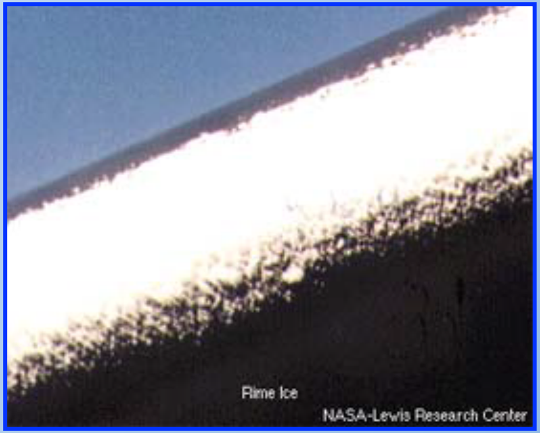
- Rime:
  - small droplets.
  - brittle and opaque, milky appearance. rapid freezing after droplet impact with growth into the airstream.
  - easier to remove than glaze.



- Mixed:
  - variable droplet size.
  - combination of glaze and rime ice.

M.K. Politovich, "Aircraft Icing" in Encyclopedia of Atmospheric Sciences, Academic Press, Oxford, 2003, 68-75.
H.E Addy Jr., M.G. Potapczuk, and D.W. Sheldon, "Modern Airfoil Ice Accreations", NASA TM 107423, 1997.

Innovation

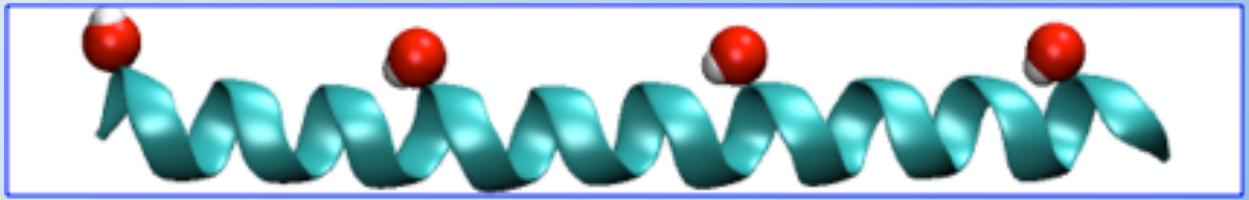
The innovation is in the combined effort of synthesis, characterization, and experimental evaluation along with molecular dynamics (MD) simulations to understand and develop ice mitigating surface coatings based on hydrogen-bonding (HB) groups and molecular roughness.

Impact if Implemented

Would provide a passive approach that would mitigate ice adhesion during the entire aircraft flight profile thus improving safety, minimizing the use of environmentally unfriendly chemicals, and reducing operational complexity.

Technical Objective

Develop surface modifying chemistries designed to mimic antifreeze protein behavior with respect to ice growth inhibition.



Antifreeze protein with regularly spaced alcohol functionality.

- Characteristic behavior:
  - thermal hysteresis: reduction in freezing point.
  - ice recrystallization inhibition.
  - ice structuring (change in ice crystal morphology).

S. Deville, C. Viazzi, and C. Guizard, "An Ice-Structuring Mechanism for Zirconium Acetate", Langmuir, 28 (2012) 14892-14898.

Technical Approach

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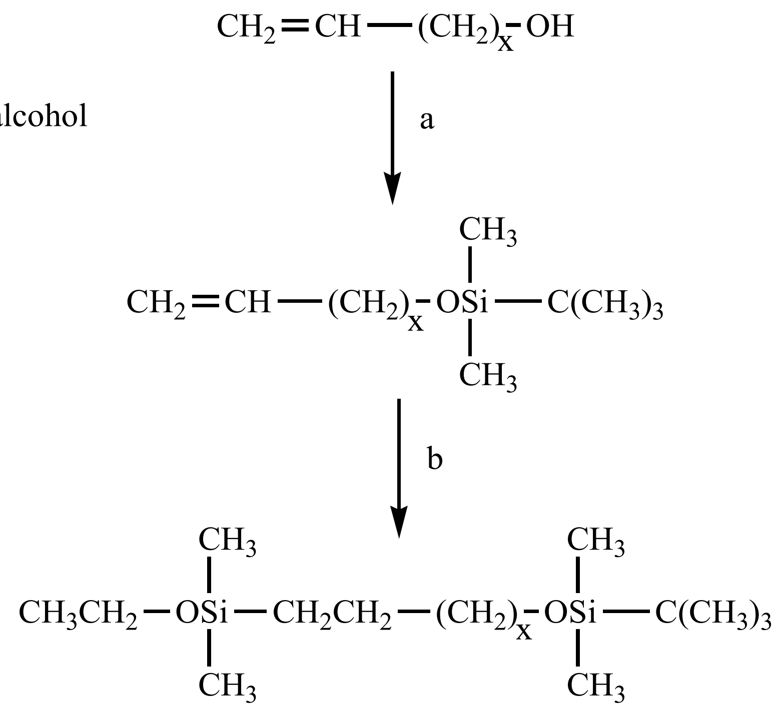
- Material synthesis and characterization of HB compounds.
- Preparation and characterization of coated Al surfaces.
- Qualitative icing studies.
  - Sub 0°C freezer.
  - Microdroplet/Temperature Monitoring Device.
- MD simulations providing information with regards to coating-ice interactions.

Accomplishments

Material Synthesis

Protection of alcohol

Hydrosilation



$x = 2, 8, 9$

a) t-butyldimethylchlorosilane, toluene, dimethylformamide, imidazole, nitrogen, room temperature
b) ethoxysilane, 10% palladium on carbon, room temperature

Accomplishments

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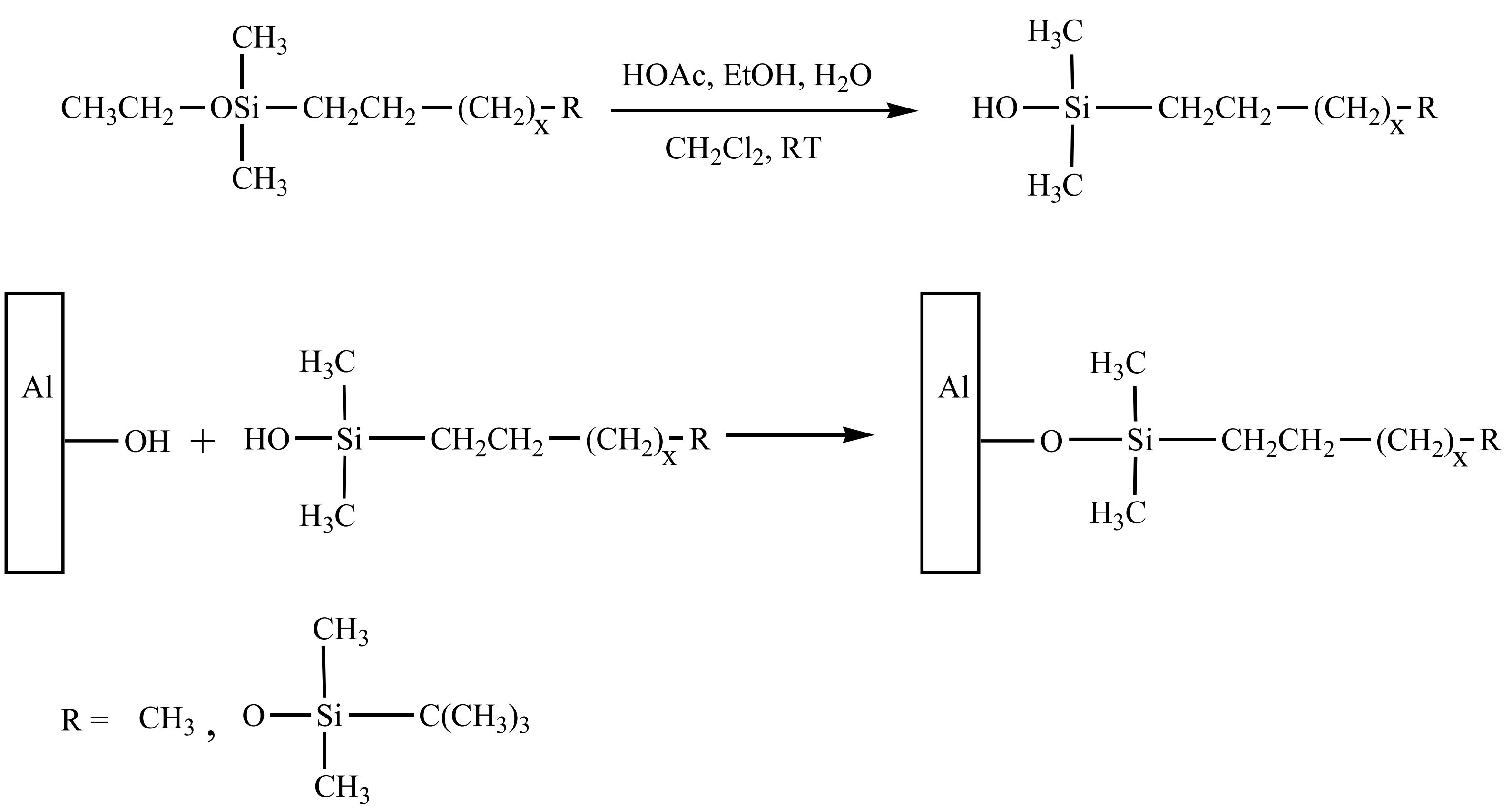
Coating Al Surface



Accomplishments

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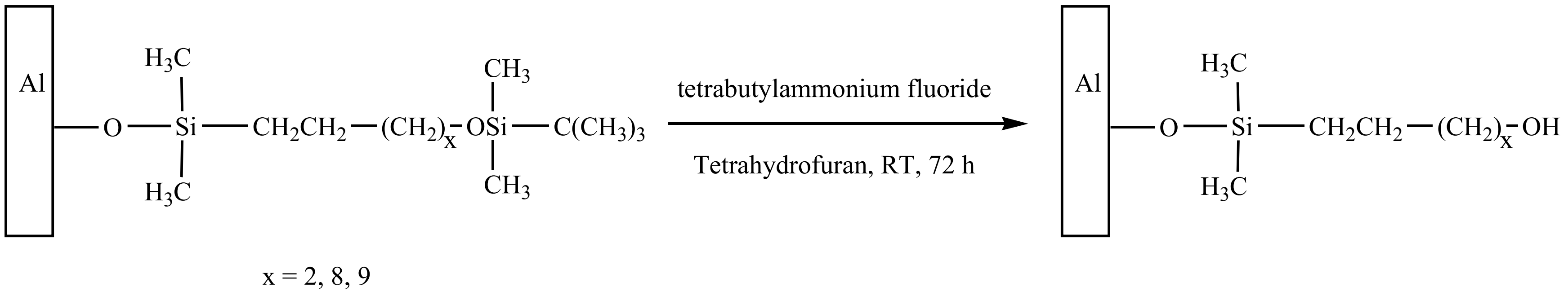
Deprotection of HB Group



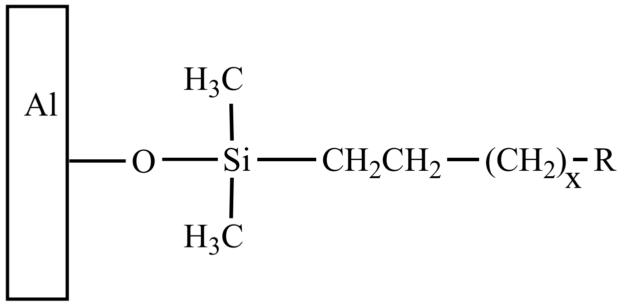
Surface	Water Contact Angle,°	
	Protected	Deprotected
C10	101.0	74.9
C11	108.0	69.6

Accomplishments

NARI

Compositions

Aliphatic (A)	Hydroxy (H)	Hydroxy/Aliphatic (H/A)
100% C3A	100% C4H	50% C4H/50% C3A
100% C7A	100% C10H	50% C4H/50% C7A
100% C11A	100% C11H	25% C10H/75% C7A
25% C11A/75% C3A	50% C4H/50% C10H	50% C10H/50% C7A
50% C11A/50% C3A	50% C4H/50% C11H	75% C10H/25% C7A
75% C11A/25% C3A	50% C10H/50% C11H	50% C11H/50% C11A
50% C11A/50% C7A		



A: R = CH_3, x = 1 (C3A), 5 (C7A), 9 (C11A)
H: R = OH, x = 2 (C4H), 8 (C10H), 9 (C11H)

Accomplishments

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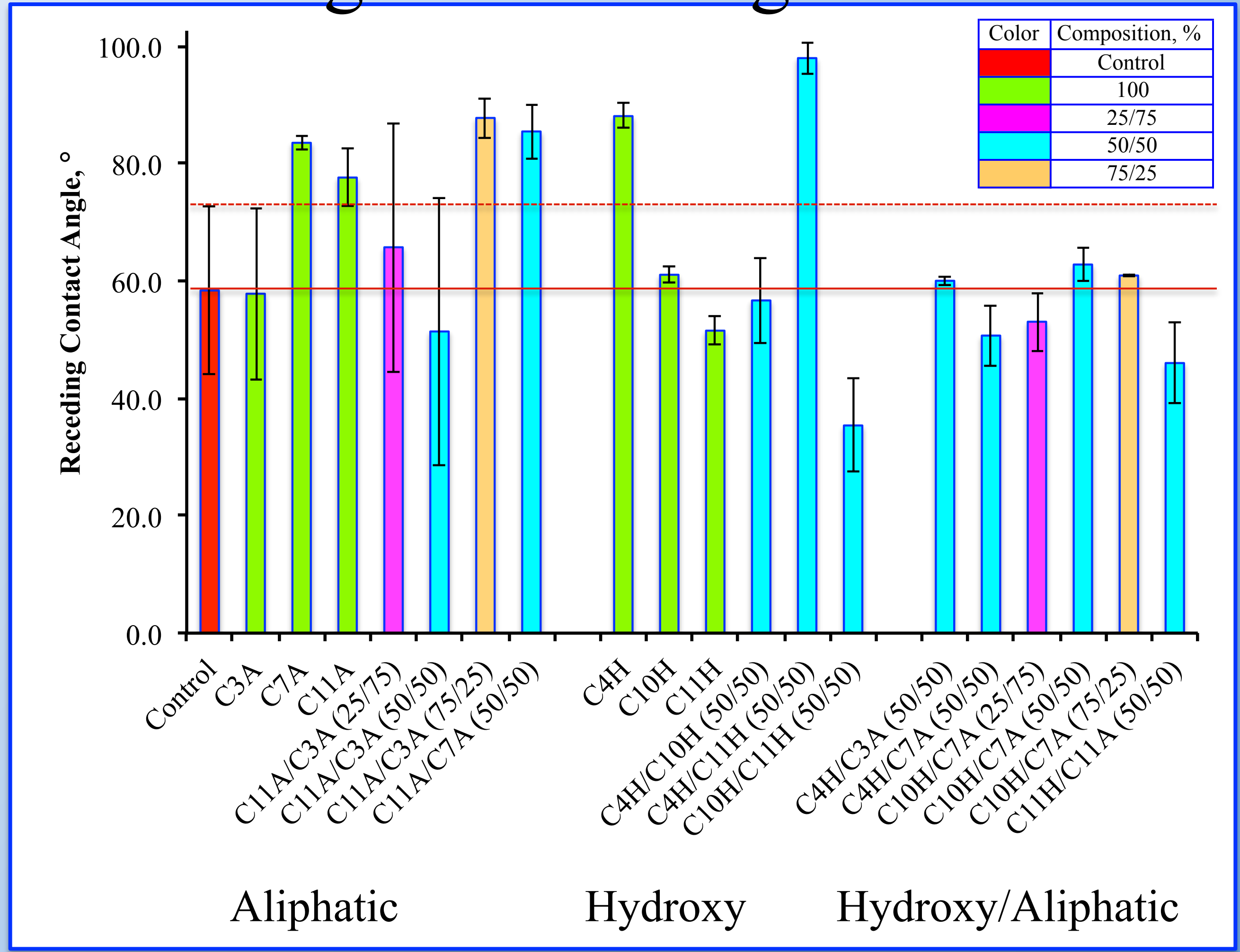
Receding Contact Angle for Water



Meuler et. al. suggest high receding contact angle for water is equated with decreased ice adhesion strength.

Caveat - Does not take into account molecular roughness.

A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley, and R.E. Cohen, “Relationships between Water Wettability and Ice Adhesion”, ACS Appl. Mater. Interfaces, 2 (2010) 3100-3110.

Accomplishments

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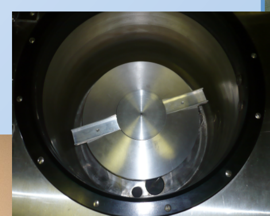
Icephobic Testing

The relationship between ice accretion, adhesion and shedding is complex and poorly understood: few published results, substantial scatter, etc.

Temperature, substrate properties and formation mechanism are all known to affect adhesion.



Many experimental methods are available to measure adhesion. Cost and complexity of the methods is proportional to TRL.

Accomplishments

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Sub 0°C Freezer Studies

- Qualitative.
- Static Test (-10 to -20°C).
- Samples preconditioned at sub-zero temperature.
- Spray coated with super-cooled distilled water.
- Visually assessed after standing several hours at temperature.

50/50 C11A/C7A

Control

Samples exhibit similar appearance to glaze (clear) ice. Test conducted at -10°C

Accomplishments

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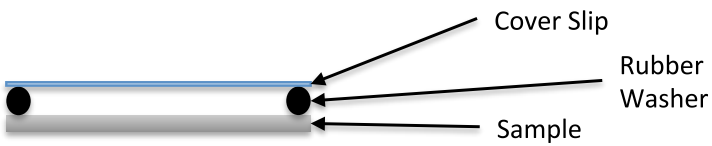
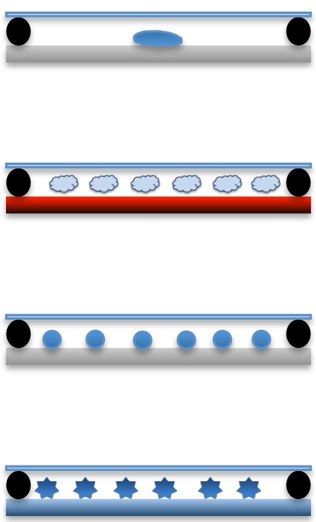
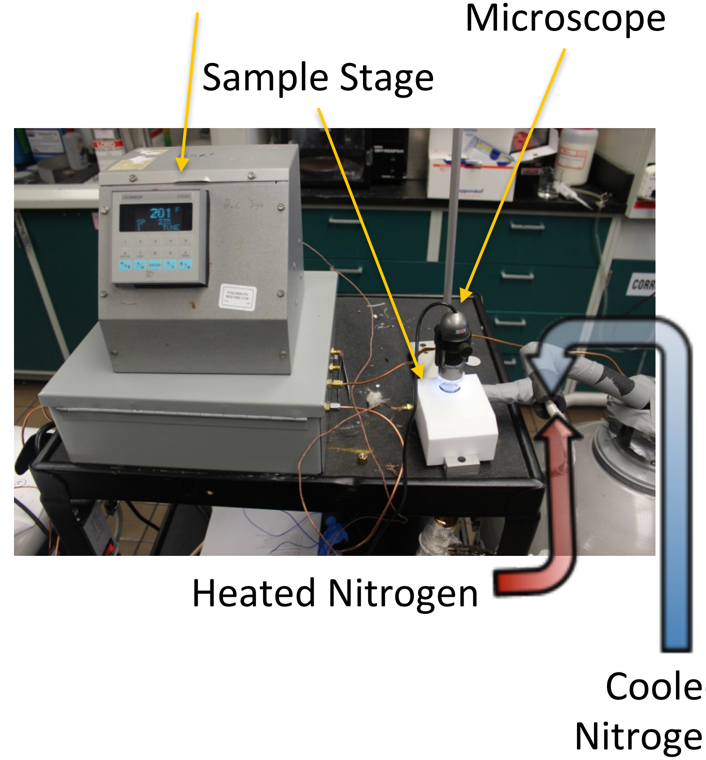
Microdroplet/Temperature Monitoring Device

Microdroplet Freezing Apparatus Schematic





- Deionized water (μLs) is placed in test chamber.
- Sample is heated to vaporize water.
- Sample is cooled, water condenses on surface in microdroplets.
- Sample cooling continues until microdroplets freeze.



Based on literature example: *Langmuir*, *28* (2012) 10749-10754. Designed by R. Penner and D. Working.

Accomplishments

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MD Simulations

Examining the effect of HB groups and molecular surface roughness upon the ice-surface interface and quasi-liquid layer (QLL) as determined from simulations monitoring density, mean squared diffusion, and structure factor as performed under constant temperature and pressure.

- QLL
  - Water at the interface between ice and the substrate surface.
  - A large QLL may minimize ice adhesion strength, thus enabling ice crystals to be readily shed by drag during flight.

- Density
  - Measured from total number of water molecules in a simulation block of known volume.
  - Value determines whether simulation block is ice or QLL.

Accomplishments

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MD Simulations

- Mean Squared Diffusion (MSD)
  - Measures general mobility of water molecules.
  - Based on Einstein-Stokes equation.
  - Smaller values indicates low mobility due to crystalline (i.e. ice) state.
  - Higher values indicate high mobility due to freedom of movement (liquid).

- Structure Factor (F_4)
  - Characterizes hydrogen-bonding network.
  - Looks at dihedral angle between two neighboring water molecules.
  - Equation based on a cosine relationship.
  - F_4 = -0.40 for ice and -0.04 for water.

Accomplishments

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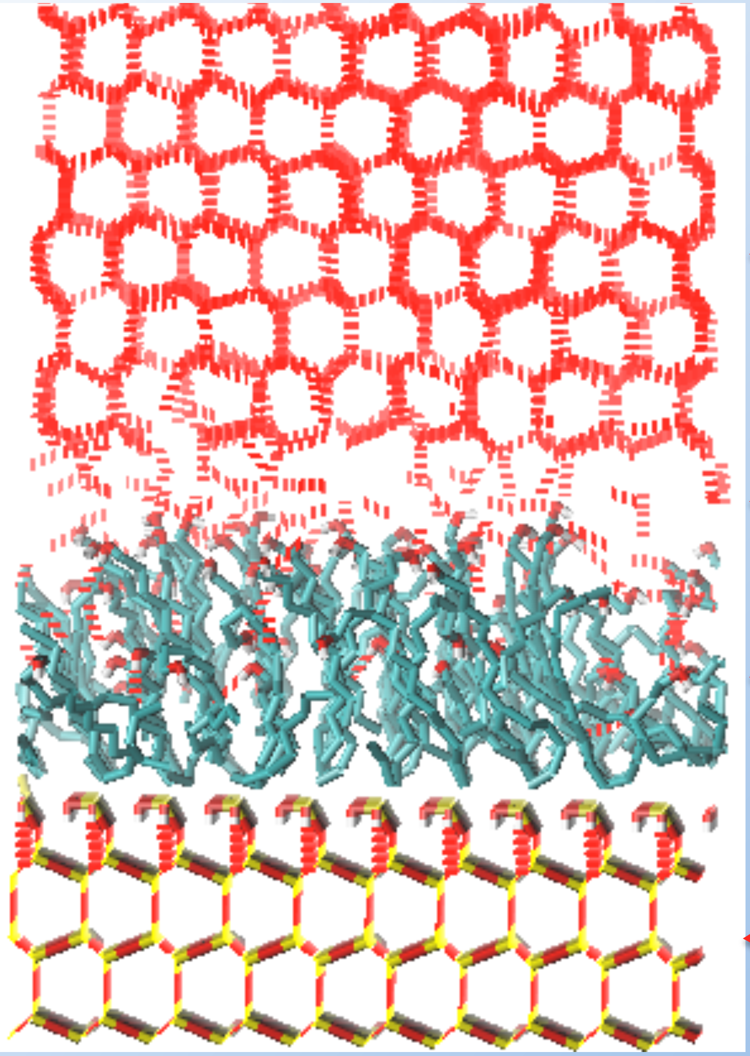
Model Configuration



Ice – 3360 waters.

QLL – length measured by density, MSD, and F_4.

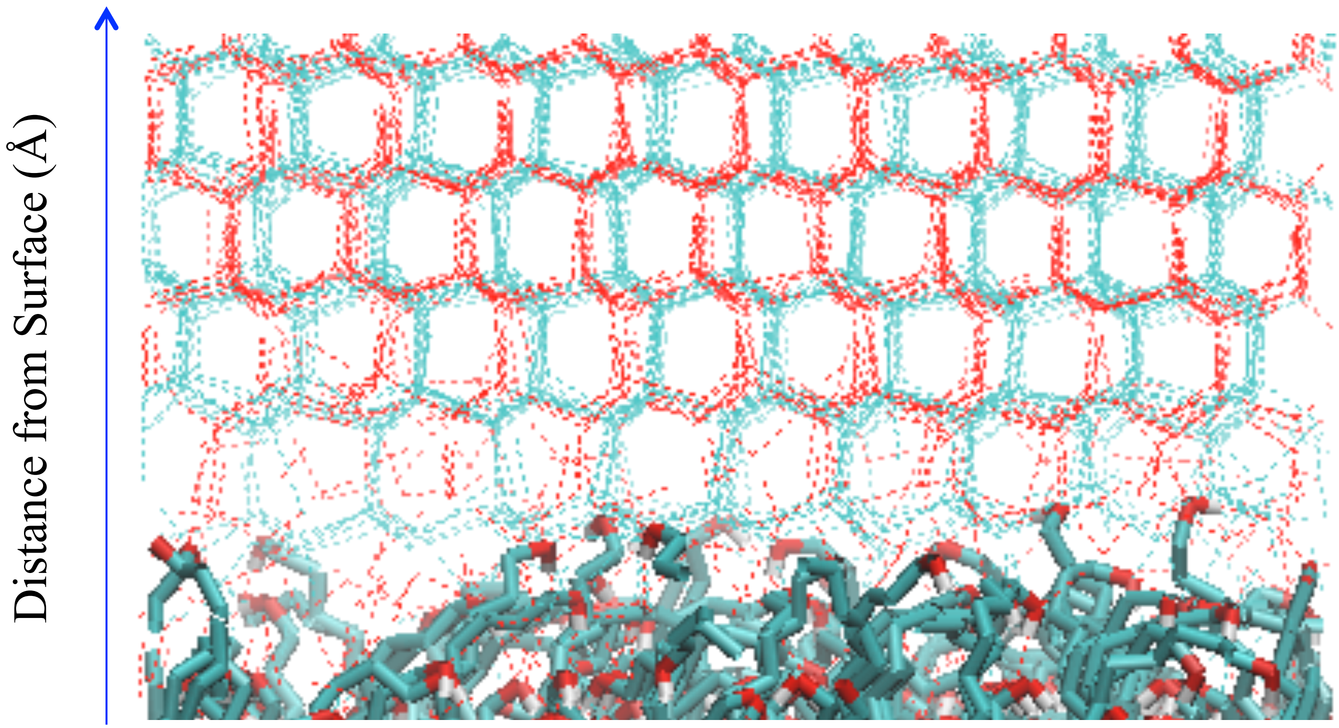
Chains on surface – 100.

Silica crystal as substrate.

Accomplishments

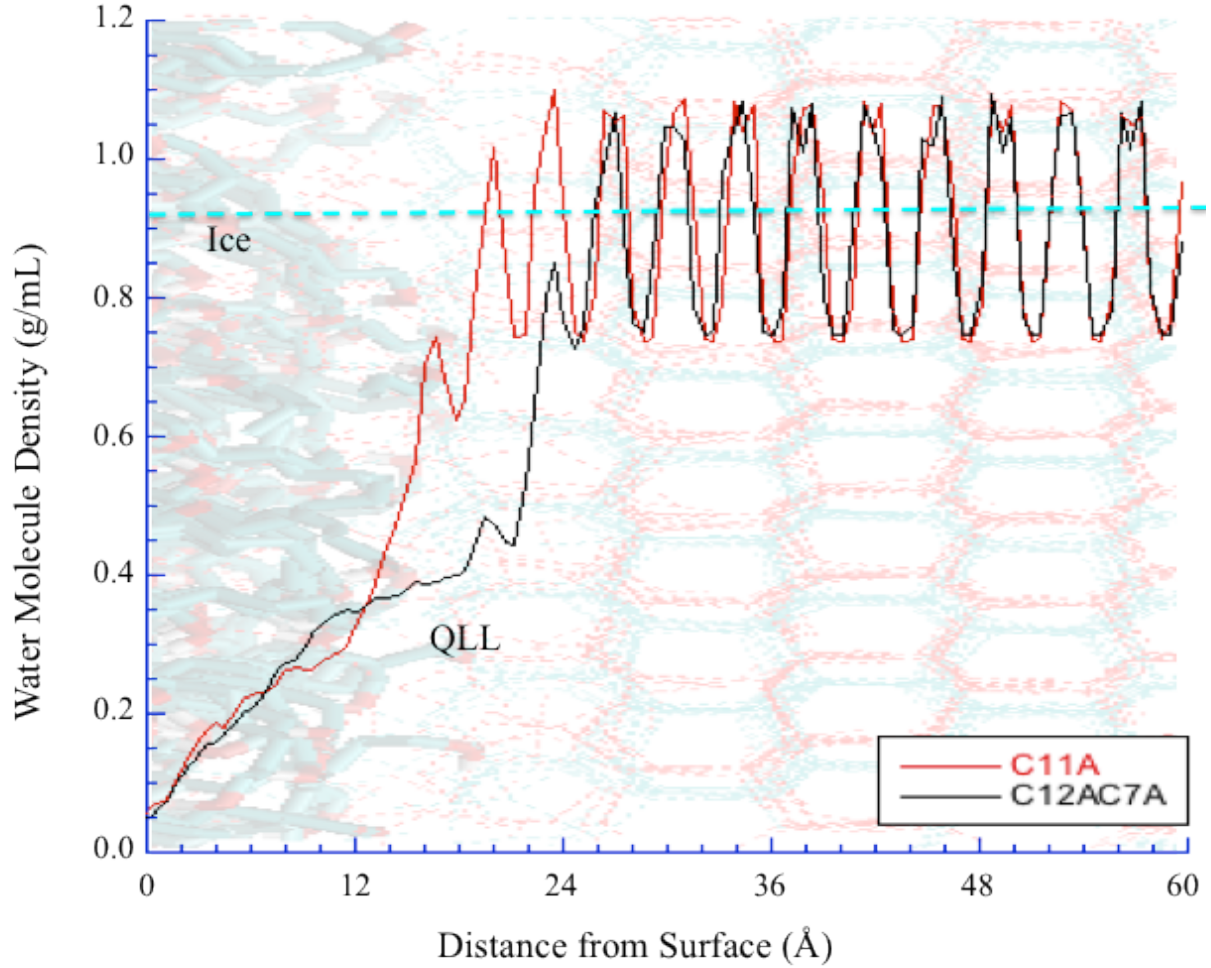
Quasi-Liquid Layer (QLL) Growth

- Blue HB network – initial ice structure
- Red HB network – after QLL develops



Accomplishments

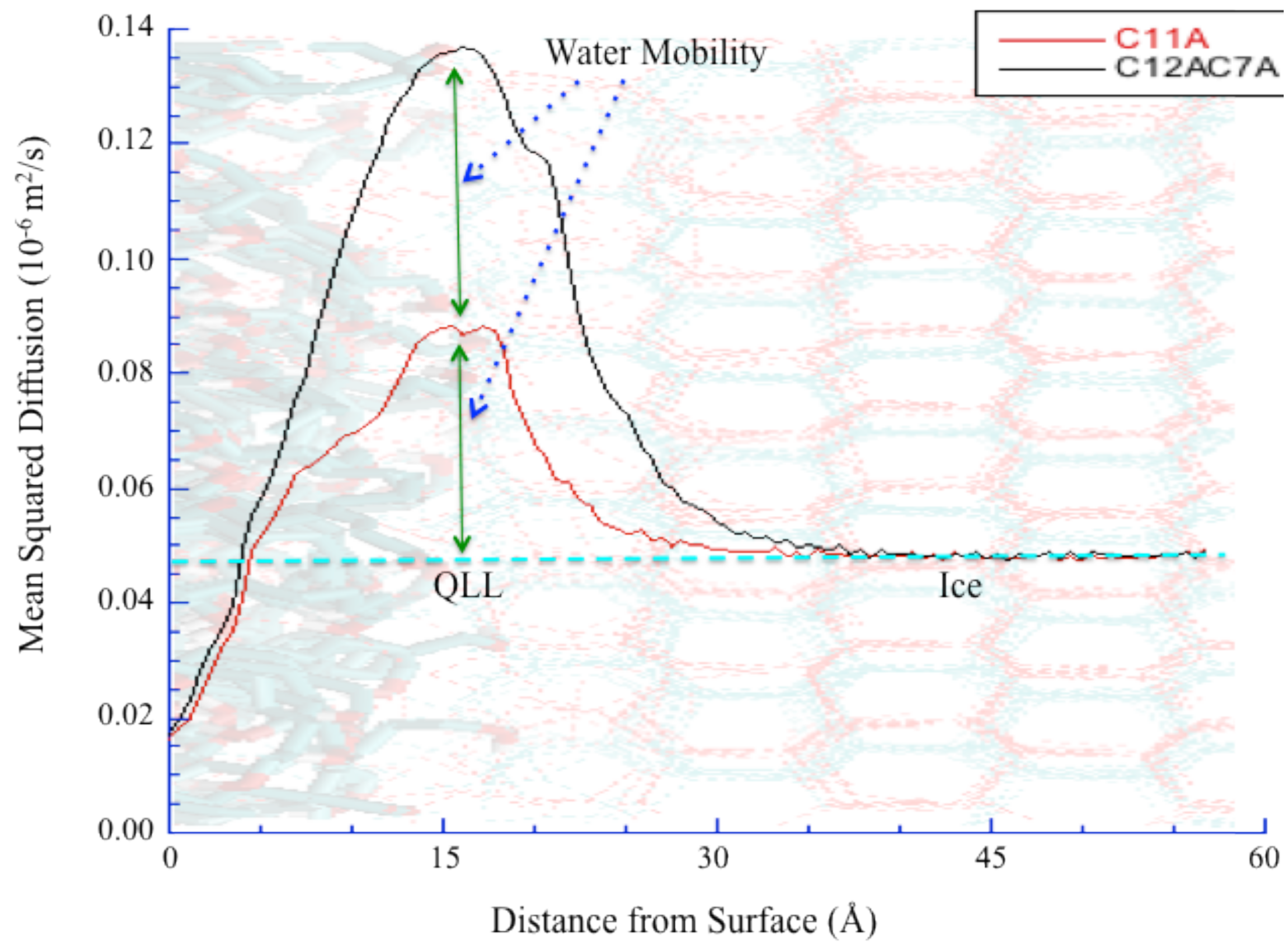
NARI



QLL thickness enhanced by mixed composition.

Accomplishments

NARI



QLL thickness enhanced by mixed composition.

Accomplishments

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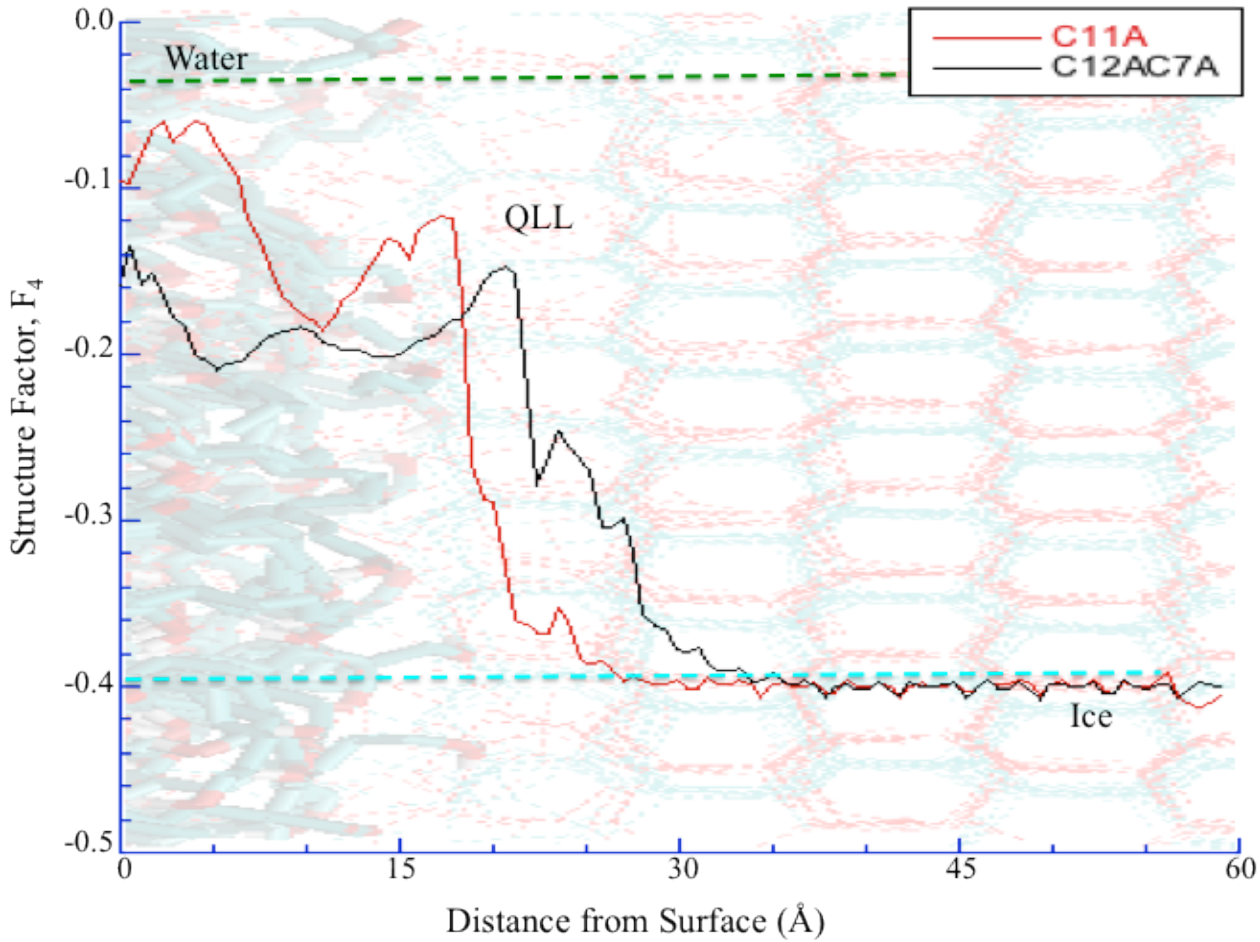

QLL thickness enhanced by mixed composition.

Accomplishments

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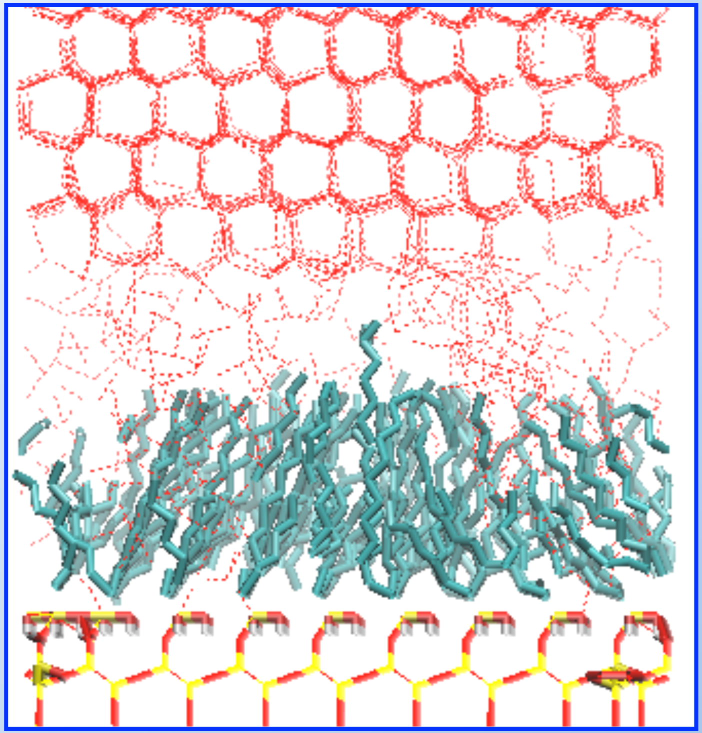
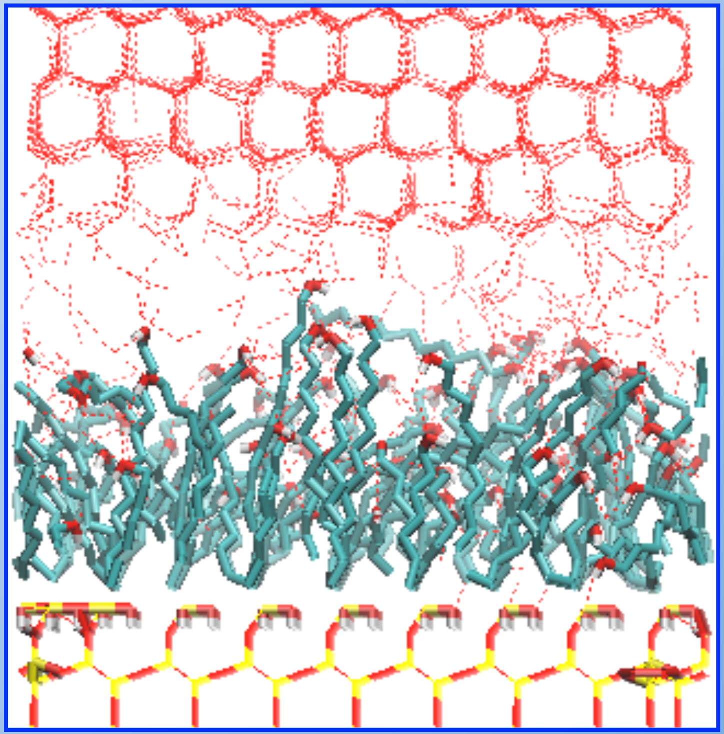
Effect of Hydrogen-Bonding on QLL

C12A/C7A



C12H/C7H



QLL thickness enhanced by mixed composition and HB groups.

Summary of Phase I Results

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- Target HB materials were synthesized, characterized, and used to coat Al surfaces for subsequent icing studies.
- Receding water contact angles and surface energies were determined using contact angle goniometry.
- Literature equates low receding contact angles for water with higher ice adhesion strength. However it does not account for molecular surface roughness.
- Qualitative icing studies initiated. Test methodology being developed.
- MD simulations
  - Heuristics established.
  - Mixtures of different chain lengths and HB groups provide enhanced QLL formation due to induced molecular surface roughness and HB.
  - Enhanced QLL may result in lower ice adhesion strength contrary to literature.

Distribution/Dissemination

NARI

Abstract entitled "**Effect of Hydrogen-Bonding Surfaces On Ice"** submitted to the 2013 American Institute of Chemical Engineers (AIChE) Annual Meeting entitled "Global Challenges for Engineering a Sustainable Future" to be held November 3-8, 2013 Hilton San Francisco Union Square, San Francisco, CA.

Next Steps (Phase II Proposal)

NARI

Goal is to design an ice mitigating polymeric coating using a building block approach.

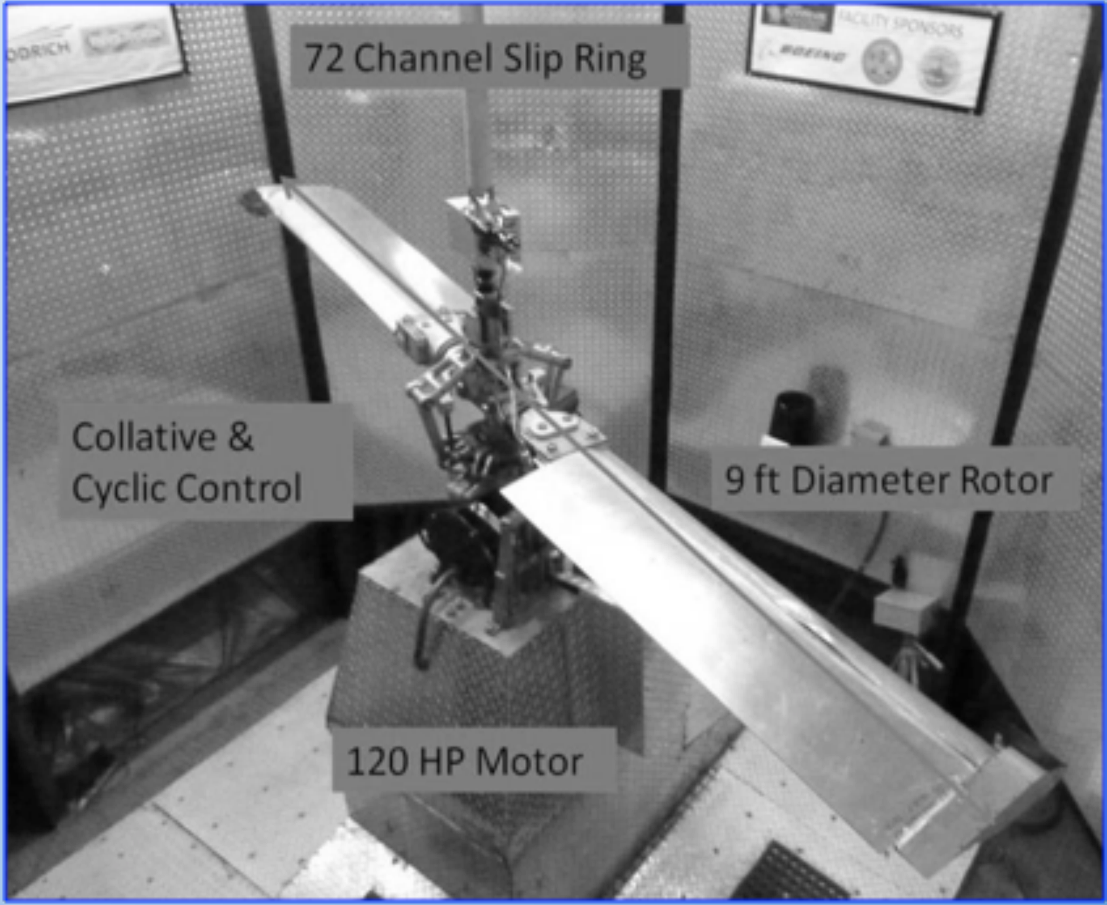
- Prepare and characterize Al substrates coated with mixtures of simple compounds containing HB and non-HB groups that are present in polymers.
- Perform icing (qualitative) and ice shear adhesion (quantitative) studies of coated Al substrates with comparison to uncoated Al.
- Determine if qualitative tests can be used for screening based on quantitative ice adhesion studies.
- Use knowledge gained from simple compound results to design ice mitigating polymeric coatings with desired attributes (i.e. QLL enhancement).
- Determine effectiveness of designed polymeric coatings with regards to ice adhesion.
- MD simulations of surfaces functionalized with various HB and non-HB groups present in simple compounds and designed polymeric coatings in presence of ice.

Next Steps (Phase II Proposal)

NARI

Adverse Environment Rotor Test Stand

- Pennsylvania State University.
- Simulated icing conditions conducted at -7 to -20°C using super-cooled water that is injected into the test chamber.
- Ice adhesion determined via shear strength measurements.



J. Soltis, J. Palacious T. Eden, and D. Wolfe, "Evaluation of Ice Adhesion Strength on Erosion Resistant Materials", 54th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Apr 8-11, 2013, Boston, MA, AIAA 2013-1509